CHEMICAL, MINERALOGICAL, AND PHYSICAL PROPERTIES OF MARTIAN DUST AND SOIL.

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Introduction: Global and regional dust storms on Mars have been observed from Earth-based telescopes, Mars orbiters, and surface rovers and landers. Dust storms can be global and regional. Dust is material that is suspended into the atmosphere by winds and has a particle size of 1-3 μm [1-4]. Planetary scientist refer to loose unconsolidated materials at the surface as "soil." The term ''soil'' is used here to denote any loose, unconsolidated material that can be distinguished from rocks, bedrock, or strongly cohesive sediments. No implication for the presence or absence of organic materials or living matter is intended. Soil contains local and regional materials mixed with the globally distributed dust by aeolian processes [5,6].

Loose, unconsolidated surface materials (dust and soil) may pose challenges for human exploration on Mars. Dust will no doubt adhere to spacesuits, vehicles, habitats, and other surface systems. What will be the impacts on human activity? The objective of this paper is to review the chemical, mineralogical, and physical properties of the martian dust and soil.

Chemical Properties: A host of lander and orbital missions have characterize the chemical composition of dust and soil. We will primarily focus on the results from the Alpha Particle X-ray Spectrometer (APXS) onboard the Mars Exploration Rovers *Opportunity* and *Spirit*. *Opportunity* has characterized the surface chemistry at Meridiani Planum for over 13 years, and *Spirit* obtained equivalent data over 6 years in Gusev crater. Basaltic soil and dust at all landing sites (Pathfinder, Spirit, Opportunity, and Curiosity) have similar compositions [6,7]. There are subtle differences in the alkaline and alkali earth cations, primary a reflection of different local basaltic mineralogies, e.g., feldspar vs. mafic mineralogy. Also, some soil shows enrichments of the local bedrock, e.g., the soil Doubloon in Gusev crater has elevated P from eroded high-P materials from the Wishstone/Watchtower rock classes [8].

Basaltic soil and dust on Mars have a composition similar to the average crustal composition [9]; however, soil and dust have enrichments in S and Cl (Table 1, [5,10]). Dust has a bit more Zn than soil (Table 1). The dust composition in Table 1 was derived from bright, undisturbed soils Desert_Gobi (Gusev crater) and MontBlanc_LesHauches (Meridiani Planum), from opposite sides of the planet. These surface materials have among the highest concentrations of nanophase iron oxides (npOx, see next section) and are thus our current best analyses of global aeolian dust [5]. Sulfur,

Cl, and npOx have strong correlations in soil and dust (Fig. 1). These elements and phases are enriched in dust (Tables 1 & 2), suggesting that they are major components of the global dust. Recently, Berger et al. [10] have characterized the chemistry of materials collecting on the science observation tray onboard the *Curiosity* rover. These measurements by APXS confirmed that martian dust is enriched in S, Cl, and Fe compared to average Mars crustal composition and soil.

Several unusual soils were discovered by *Spirit* while dragging a wheel through soil in Gusev crater. The Paso Robles class soil has high SO_3 (~35 wt. %, Table 1) and the Kenosha Comets soil subclass contained very high SiO_2 (~90 wt. %, Table 1) [8]. Although these types of soils are not common at other landing sites, human missions might encounter these unusual soils.
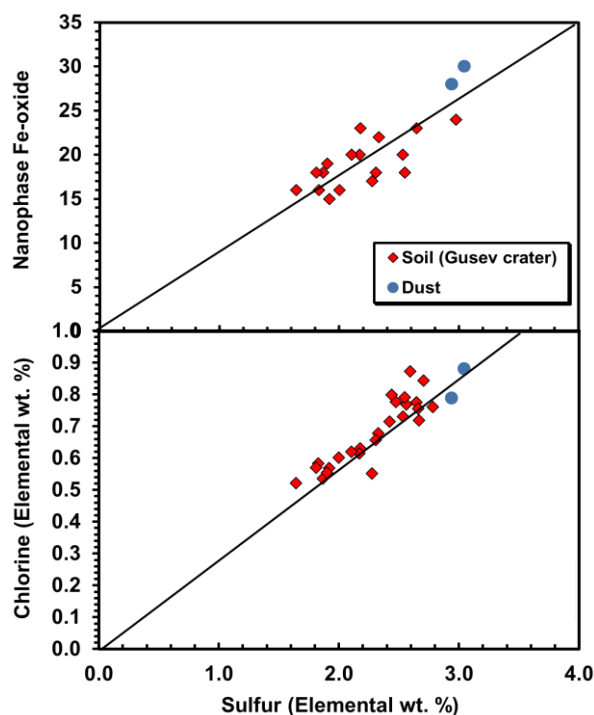

Figure 1. Sulfur, chlorine, and nanophase iron oxide (npOx) contents in Mars soil and dust. Note the higher S, Cl, and npOx in martian dust. These three phases correlate in soil and dust.

Next, we address two aspects of dust chemistry that may have impacts on human exploration – oxychlorine

Table 1. *Average compositions of the Martian crust, soil, and dust. Maximum oxide/elemental compositions discovered so far in soil on Mars along with locations are listed in the last two columns.*

Oxide/ Element	Average Mars Crust [9]	Average Mars Soil (Gusev Crater Panda Subclass; [5])	Average Mars Dust [5]	Max. from MER Surface Missions	
				Maximum [8]	Location
	------------------wt.%----------------------			wt.%	
SiO_2	49.3	46.52 ± 0.57	44.84 ± 0.52	90.53	Kenosha Comets, Gusev crater
TiO_2	0.98	0.87 ± 0.15	0.92 ± 0.08	1.90	Doubloon, Gusev crater
Al_2O_3	10.5	10.46 ± 0.71	9.32 ± 0.18	12.34	Cliffhanger, Gusev crater
FeO	18.2	12.18 ± 0.57	7.28 ± 0.70	4.41	Paso Robles, Gusev crater
Fe_2O_3		4.20 ± 0.54	10.42 ± 0.11	18.42	
MnO	0.36	0.33 ± 0.02	0.33 ± 0.02	0.36	The Boroughs, Gusev crater
MgO	9.06	8.93 ± 0.45	7.89 ± 0.32	16.46	Eileen Dean, Gusev crater
CaO	6.92	6.27 ± 0.23	6.34 ± 0.20	9.02	Tyrone, Gusev crater
Na_2O	2.97	3.02 ± 0.37	2.56 ± 0.33	3.60	Cliffhanger, Gusev crater
K_2O	0.45	0.41 ± 0.03	0.48 ± 0.07	0.84	Bear Island, Gusev crater
P_2O_5	0.90	0.83 ± 0.23	0.92 ± 0.09	5.61	Paso Robles, Gusev crater
Cr_2O_3	0.26	0.36 ± 0.08	0.32 ± 0.04	0.51	Tyrone, Gusev crater
Cl	-	0.61 ± 0.08	0.83 ± 0.05	1.88	Eileen Dean, Gusev crater
SO_3	-	4.90 ± 0.74	7.42 ± 0.13	35.06	Arad, Gusev crater
Element	------------------------μg/g----------------------			μg/g	
Ni	337	544 ± 159	552 ± 85	997	El Dorado, Gusev crater
Zn	320	204 ± 71	404 ± 32	1078	Eileen Dean, Gusev crater
Br	-	49 ± 12	28 ± 22	494	Paso Robles, Gusev crater

compounds (i.e., perchlorates/chlorates) and chromium.

Oxychlorine Compounds. Perchlorates were first discovered in surface soil at the Phoenix landing site near the northern polar region [11]. Since that discovery by the MECA Wet Chemistry Lab, the Sample Analysis on Mars (SAM) instrument has detected oxychlorine compounds in the soil and bedrock at the *Curiosity* landing site in Gale crater [12,13]. These author's used the term oxychlorine compounds because the SAM instrument detected the evolution of O_2, chlorinated hydrocarbons, and HCl. These gases are most likely from the thermal decomposition of perchlorates, chlorates, and/or chlorites [13-15]. Although, no instruments onboard *Curiosity* have the capability to detect these anions, the temperatures of evolved O_2 are consistent with thermal decomposition of perchlorate/chlorate salts of Fe, Mg, and Ca [13-16]. The amount of perchlorate measured at the Phoenix landing site was about 0.6 wt. %, which would be equivalent to about 1 wt. % perchlorate salt [11]. The amount of perchlorate estimated from the evolved O_2 in a Gale crater windblown deposit (Rocknest) was ~0.4 wt. % (Fig. 2, [12]), similar to what was measured by the Phoenix lander. The maximum perchlorate concentration inferred by evolved O_2 in an outcrop was ~1.1 wt. % Cl_2O_7 in a mudstone (Cumberland) in Gale crater [13]. Oxychlorine compounds (e.g., perchlorates) present in Gale crater soils and sediments have complicated the detection of organic molecules, which are combusted during pyrolysis and thermal decomposition of oxychlorine compounds during SAM evolved gas analyses [12-14]. These oxychlorine compounds may also present challenges for human health and engineering performance to hardware and infrastructure (e.g., corrosion during heating of surface soil for IRSU water extraction).

Chromium. Another concern for human missions is the element chromium (Cr). Past advisory groups to NASA have raised the possibility of the presence of Cr^{6+} in dust and soil and that, if present in sufficiently high concentrations, it could be deleterious to human
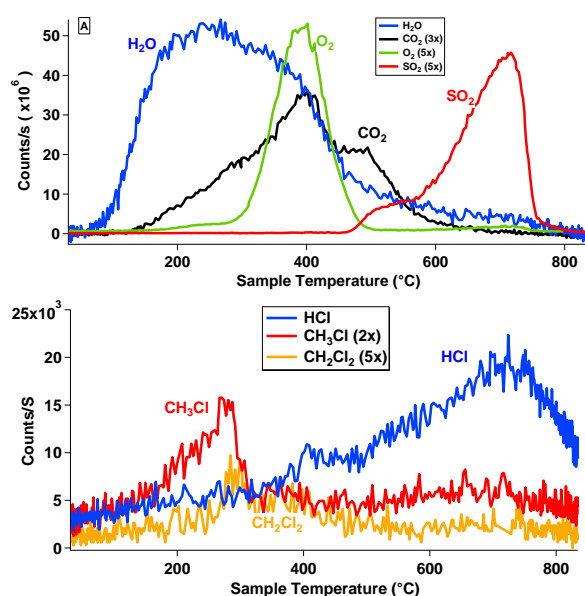
Figure 2. *Gases released during Sample Analysis at Mars (SAM) pyrolysis of the Rocknest windblown deposit in Gale crater [12]. The evolution of O_2, chlorinated hydrocarbons, and HCl suggests the thermal decomposition of an oxychlorine compound (e.g., perchlorate). Water is the most abundant gas released (~2 wt. % H_2O). High temperature SO_2 release may be the thermal decomposition of sulfides. Fine-grained Fe- or Mg-carbonate may be the source of some of the evolved CO_2.*

health [17]. We present here evidence that Cr^{6+} is highly unlikely in dust and soil. A Mössbauer spectrometer was one of the science instruments onboard the Mars Exploration Rovers that landed and analyzed surface materials at Gusev Crater and Meridiani Planum. The instrument detects only the element iron (Fe) and is separately sensitive to its oxidation state (e.g., Fe^{6+}, Fe^{3+}, Fe^{2+}, and Fe^0), coordination state (e.g., octahedral and tetrahedral), and mineralogical speciation (e.g., Fe in specific silicate, sulfide, and oxide minerals). One mission objective was to look for Fe^{6+}, the highest oxidation of Fe. No Fe^{6+} was detected in any martian surface sample, including soil and dust. Using detection limits based on counting statistics, a conservative upper limit for the Fe^{6+} concentration is 1-2% (relative) of the total Fe concentration, or about 0.2 to 0.4 wt.% for typical martian basaltic soil and dust. Assuming the same efficiency for oxidation of Cr^{3+} to Cr^{6+}, the upper limit for the Cr^{6+} concentration in typical basaltic soil is 0.003 to 0.005 wt.% using 0.32 wt.% for the total Cr concentration. Note, however, that both Fe^{6+} and Cr^{6+} are not stable in the presence of Fe^{2+}, which is abundant in martian surface materials.

Mineralogical Properties: The mineralogy of Martian dust and soil is based upon Mössbauer and Mini-TES instruments onboard *Spirit* and *Opportunity* and the CheMin X-ray diffraction instrument onboard *Curiosity*. The Mini-TES instrument indicated the presence of plagioclase feldspar in dust and soil [18]. The Mössbauer spectrometer has detected npOx in the dust and soil (Fig. 3, [5]). The npOx component can include several phases, including superparamagnetic forms of hematite and goethite, lepidocrocite, akaganeite, schwertmannite, hydronium jarosite, ferrihydrite, iddingsite, and the Fe^{3+} pigment in palagonitic tephra [5, 19-21]. Other Fe-bearing phases in the soil include the basaltic minerals olivine, pyroxene, ilmenite, and magnetite [5].

The CheMin instrument has analyzed two surface "soils" in Gale crater, a windblown deposit called Rocknest and an active aeolian dune called Bagnold. We will only present the Rocknest X-ray diffraction data here because it contains a larger amount of the global dust component. The CheMin instrument accepts materials less than 150 μm in diameter through the sample processing system on *Curiosity*. Rocknest contains basaltic minerals along with several alteration phases (Table 2, [22]). The major alteration phase in Rocknest is an X-ray amorphous component that includes the npOx phase(s) [6]. The amorphous phase also contains the S- and Cl-bearing volatile phases described above (e.g., oxychlorine compounds, sulfides, sulfates). There is still a large fraction of Si in the amorphous phase that may be a secondary alteration silicate; however, we cannot rule out the possibility of unaltered volcanic or impact glass [6,23]. Other alteration phases in the Rocknest soil are Ca-sulfate (anhydrite) and hematite.

Physical Properties: We will limit our physical properties discussion of surface soil and dust to an overview. Edgett [24] presents a detailed analysis of the particle sizes and shapes of surface silts and sands in soil at the Gale crater landing site at this workshop. Microscopic imagers have flown on landed missions. The spatial resolution of the Microscopic Imagers (MI) on *Spirit* and *Opportunity* was ~30 μm, and the resolution of the Mars Hand Lens Imager (MAHLI) on *Curiosity* was ~15 μm [24-26]. The Optical Microscope (OM) on the Mars Phoenix Lander had resolution of 4 μm and could resolve particles of about 10 μm and larger. Phoenix also included an Atomic Force Microscope (AFM) that was part of the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA) payload that could resolve the shape of individual dust particles down to about 100 nanometers in size. A key disadvantage of imagers on the Phoenix lander was the lack of mobility; the lander was restricted to obtaining materials in the area the Robotic Arm could reach.

Table 2. *Quantitative mineralogy of the Rocknest windblown deposit (soil) in Gale crater [22].*

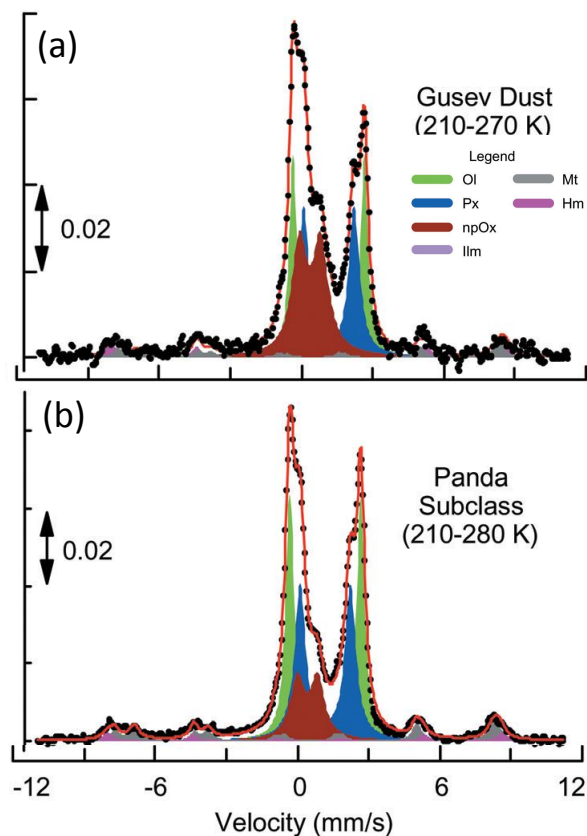| Mineral	Rocknest Windblown Deposit
	---------------Wt. %-----------------
Feldspar	26
Olivine	13
Pyroxene	20
Magnetite	2
Hematite	1
Anhydrite	1
Quartz	1
Ilmenite	1
X-ray Amorphous	35

Figure 3. *Mössbauer spectra for the (a) martian dust and (b) soil (Panda subclass is representative of Mars average soil composition [5]). Note the larger peaks for the nanophase Fe-oxides (np-Ox) in the dust indicating more np-Ox in the dust [legend: Ol = olivine, Px = pyroxene, npOx = nanophase Fe-oxide, Ilm = ilmenite, Mt = magnetite, Hm = hematite].*

Particle size distribution. Particle size distributions of soil is poorly constrained because microscope resolution can only resolve coarse silt, sand, and larger grains. Pike et al. [27] were able to provide a particle size distribution for Phoenix surface materials by using a combination of the OM and AFM. Only about 1 vol. % of the material delivered to the AFM had a particle size less than about 4 μm. This low volume percent of clay-sized particles seems unreasonable for other soils on Mars based on alteration mineralogy and chemistry. Here, we use a combination of the CheMin X-ray amorphous and Mössbauer Fe mineralogy to provide constraints of clay-sized materials in soil encountered at rover landing sites. We assume that the npOx is in the clay-size fraction and a portion of the X-ray amorphous component is similarly sized. About 15 % of the Fe in typical Mars soil (e.g., Panda class) is in the form of npOx [5]. This amount of npOx would be equivalent to about 3 wt. % clay-sized materials based on a total FeO content of 16 wt. %. This amount of npOx would place the lower limit of clay-sized particles at about 3 wt. %. The estimated amount of X-ray amorphous materials in Rocknest windblown deposit is about 35 wt. % [22]. This fraction includes the poorly crystalline npOx phases. An upper limit on the total amount of clay-sized materials would be 35 wt. % assuming all of the X-ray scatter results from very fine particles, i.e., significantly less than 4 μm in size. We can estimate that about 21 % of the soil materials have been altered by chemical alteration based on the Fe^{3+}/Fe_{Total} of 0.21 determined by Mossbauer spectroscopy on typical Mars soil although some of the Fe^{3+} could be in magnetite [5]. So it is reasonable to estimate the clay fraction in soil to be 15-25 wt. % and about 75-85 wt. % of the less than 2 mm materials in the silt and sand fractions.

Dust shape. The shape of discrete dust particles may play an important role in human health issues (e.g., dust in the lungs) and engineering performance of spacecraft parts (e.g., dust on seals). The only data we have acquired on Mars that can resolve dust particles is from the atomic force microscope (Fig. 4, [27]). Dust particles are irregularly shaped but appear to have rounded edges, possibly a result of aeolian processes.

Summary: Soil and dust on Mars have basaltic compositions, but are enriched in S, Cl, and npOx compared to crustal materials. The correlation of S, Cl, and npOx in soil/dust and their greater abundances in dust suggests that they are a component primarily associated with aeolian martian dust. The particle size of dust is about 1-3 μm. Oxychlorine compounds are found wide spread in soil/dust and are almost certainly a component of the martian dust. Chromium in soil and dust is unlikely to attain the hexavalent state and not likely to be a viable health hazard for humans.

Mineralogy of soil and dust is dominated by basaltic minerals (plagioclase feldspar, olivine, pyroxene, magnetite); however, large amounts of X-ray amorphous materials and npOx in the soil and dust suggest chemical alteration of primary basaltic materials. We estimate that about 15-25 wt. % of martian soil is composed of clay-sized materials (< 4 μm) and the shape of martian dust is irregular, but rounded edges resulting from wind processes.

Soil is produced by a combination of geologic processes including physical (impact, wind) and chemical (aqueous alteration, oxidation) processing of local and regional basaltic materials. The finest fraction of the soil, i.e., dust, is suspended by wind and has been transported at regional and global scales and remixed with surface soil. The impacts of dust and soil on human missions must be addressed, but we do not foresee any "show stoppers" based on available data.
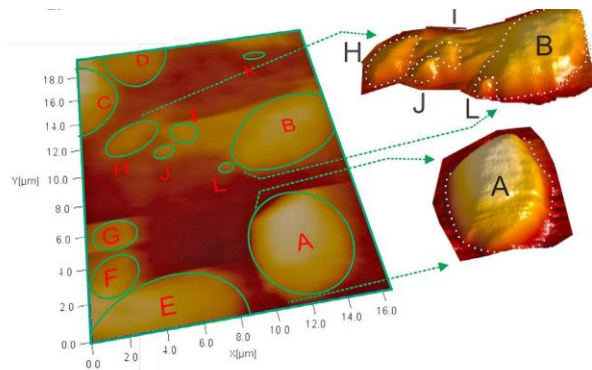

Figure 4. *Atomic Force Microscope image of a dust particle from soil materials at the Phoenix landing site [27]. Particles appear to be rounded. These particles are 2-4 μm in size.*

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